

PATENT SPECIFICATION

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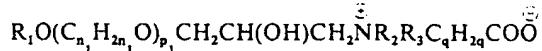
(54) A LIQUID DETERGENT COMPOSITION

(71) We, BEROL KEMI AB, formerly known as Modokemi AB, a Swedish Joint-Stock Company of S-444 01 Stenungsund, Sweden, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

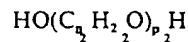
The present invention refers to liquid aqueous detergent compositions containing sequestering agents.

There are many proposals of formulating liquid detergents, but still such products have not received any decisive commercial success. Probably, this is due to the fact that one has not yet been successful in combining an efficient surfactant with sufficient amounts of sequestering agents so as to be able to achieve good washing activity. Furthermore, the product obtained should be clear and liquid within a great range of temperature.

It has now been found that one may obtain a clear liquid detergent composition with good washing effect and water solubility by utilizing, as surface-active component, an amphotolyte of the betaine type not previously known. By a 'clear' composition, we mean one which appears to be clear to the human eye on visual examination. The liquid detergent composition according to the invention contains as essential components sequestering agents, a surface-active portion and water, the surface-active portion consisting of at least one non-ionic surfactant and at least one amphotolyte of the general formula



wherein R₁ designates an aliphatic or cycloaliphatic group with 6—22 carbon atoms or an aromatic group substituted with one or more alkyl groups with a total of 4—18 carbon atoms in the alkyl groups; R₂ and R₃ independently designate alkyl groups with 1—3 carbon atoms; n₁ is 2 and/or 3 and/or 4; p₁ is an integer from 0 to 10; and q is an integer 1, 2 or 3. The weight ratio of complexing agent, non-ionic surfactant amphotolyte and water may of course vary within wide limits but generally amounts to 4—25:1—20:1—15:40—90, preferably 6—20:2—15:1—10:45—80. Detergent compositions of this constitution form a clear, liquid solution with good cleaning effect and relatively low foaming. To obtain additional foam reduction there may, if desired, be added an alkylene glycol of the general formula

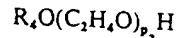


wherein n₂ is 2, 3 and/or 4, preferably 2 and/or 3, and p₂ is a number from 1 to 10, preferably 1 to 5. The amount of alkylene glycol may vary from no addition at all up to double as much as the amount by weight of the non-ionic surfactant added. In certain cases, e.g. where the nonionic surfactant is difficulty soluble and is present in a high concentration, the alkylene glycol also has a solubility-improving effect.

The sequestering agent included in the detergent composition preferably is of

inorganic nature, such as sodium or potassium pyrophosphate, sodium phosphate, sodium tripolyphosphate and sodium hexametaphosphate. Also organic sequestering agents have shown good effect in compositions according to the invention, and of this type there should above all be mentioned alkene phosphonates, salts of aminocarboxylic acids, such as ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), hydroxyethylmethylenediaminetriacetic acid (HEDTA) and diethylenetriaminopentacetic acid (DPTA), hydroxyethyl-iminodiacetic acid (HEIDA), salts of oxycarboxylic acids, such as citric acid and glyconic acid, and salts of polycarboxylic acids, such as polymaleic acid, polyitaconic acid and polyacrylic acid. The amount of the sequestering agents stated generally is 10—30% of the total weight of the composition.

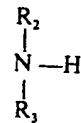
The non-ionic surfactant primarily consists of alkylene oxide adducts, and among these ethylene oxide and propylene oxide adducts of monoalkyl phenols, dialkyl phenols, fatty alcohols, secondary alcohols, alkyl amines and alkyl mercaptans should be mentioned, in which compounds the total number of carbon atoms in the hydrophobic part amounts to 8—20 carbon atoms and the poly-alkylene glycol chain comprises 5—30 alkylene glycol groups. Particularly suitable are the non-ionic compounds which are comprised by the general formula



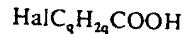
wherein R_4 designates an aliphatic or cycloaliphatic group with 8—20 carbon atoms or a mono- or dialkylphenyl with a total of 4—18 carbon atoms in the alkyl groups, and p_3 is an integer from 5 to 30, preferably from 5 to 20. Specific examples of suitable non-ionic surfactants which are comprised by this formula are ethylene oxide adducts with decyl alcohol, lauryl alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, eicosyl alcohol, oleyl alcohol, cyclooctanol, cyclododecanol, cyclohexadecanol, octyl phenol, nonyl phenol, dodecyl phenol, hexadecyl phenol, dibutyl phenol, dioctyl phenol and dinonyl phenol.

Among the amphotropic compounds which are comprised by the formula stated above those wherein the nitrogen atom and the carboxylic group are linked to the same carbon atom should be mentioned. Preferably, q designates the number 1. Furthermore, compounds wherein n_1 is 2 or wherein p_1 is O and R_2 and R_3 designate methyl groups are generally preferred.

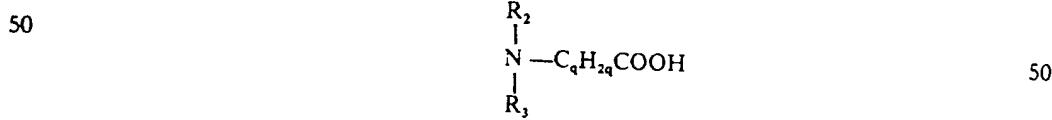
In producing the amphotropic compounds one preferably starts from an aliphatic or cycloaliphatic alcohol with 6—22 carbon atoms, or from an aromatic hydroxyl compound containing a total of 10—24 carbon atoms, to which there may, if desired, in a manner known per se, have been added ethylene oxide, propylene oxide and/or butylene oxide in an amount of 0—10 alkylene oxide units. In the case of butylene oxide, all isomers may be used. The aliphatic, cycloaliphatic or aromatic hydroxyl compound, which thus possibly contains alkylene oxide units is reacted with epichlorohydrin to the corresponding chloroglyceryl ether which is an important intermediate product. The glyceryl ether may then be aminated and quaternized either in two stages by reaction with, first, a dialkyl amine with the formula



wherein R_2 and R_3 have the meaning stated above, and then with a straight or branched chain monohalogenocarboxylic acid of the formula



wherein Hal means a halogen atom, such as bromine or chlorine, and q has the meaning stated above, or in one stage with an amino acid of the formula



wherein R₂ and R₃, and q have the meaning stated above.

Of the two reaction variants the one with amino acid is preferred, since it results practically only in compounds according to the invention. On the other hand, in the reaction between the glyceryl ether and the dialkyl amine an undesirable quaternary compound may be obtained if the amount of glyceryl ether compound is not closely controlled. Furthermore it has surprisingly been found that the glyceryl ether compound and the amino acid in the presence of alkali can be reacted with each other and give the corresponding quaternary compound in such a high yield as more than 95%.

The reaction between the hydroxyl compound, possible in the form of an alkylene oxide adduct, and epichlorohydrin is carried out at a temperature of about 100—150°C in the presence of a catalyst. As a catalyst, especially SnCl₄, BF₃, and HClO₄, have proved excellent and they give a rapid and easily controllable reaction, but also other acid catalysts, such as toluene sulfonic acid and sulfuric acid are usable. To obtain a complete reaction of the alcohol compound the epichlorohydrin is usually added in excess. The amination of the chloroglyceryl ether with the secondary amine is carried out in the presence of alkali, such as sodium hydroxide, at a temperature of 100—150°C. Usually, the reaction is carried out in the presence of a polar solvent, e.g. water or a low molecular alcohol, such as methanol, ethanol, monoethyleneglycol, diethyleneglycol, ethyldiglycol and ethylglycol. To avoid quaternization during the amination stage the molar ratio of the dialkyl amine to the chloroglyceryl ether at the initial stage should be at least 3 and the temperature at this molar ratio be not below 140°C. In the case of higher molar ratios the temperature may be lowered to 100°C. The quaternization of the tertiary amine with the halogenocarboxylic acid is carried out in a neutralized aqueous solution, the reaction temperature being 50—100°C and the reaction time about 2—6 hours. If the tertiary amine contains hydrocarbon groups having more than 14 carbon atoms it has been found advantageous to add also a glycol compound, such as ethyldiglycol, partly to increase the solubility of the amine, partly to reduce the viscosity of the reaction mixture. If the chloroglyceryl ether is reacted with amino acid the reaction is carried out at a neutral or slightly basic pH, preferably between 7 and 10. The solvent has to be polar and in principle the same solvent as at the amination with dialkyl amine may be used. The reaction temperature is suitably within the interval 50—140°C and the reaction time is from about 15 minutes to about 3 hours.

The compounds according to the invention may also be produced by several variations of the methods stated above.

Thus, the chloroglyceryl ether may be caused to react with ammonia or a primary amine having a methyl or ethyl substituent, and subsequently additional alkylene substituents may be introduced with, for example, methyl or ethyl chloride or dimethyl or diethyl sulfate. Similarly, a monoalkyl-substituted amino acid may be utilized and the quaternization carried out with some of the reactants stated above.

The processes here described are, however, more complicated than those earlier described and include more reaction stages. Besides, they result in a greater number of by-products and a lower total yield.

The aliphatic alcohols, with 6—22 carbon atoms, which are used in preparation of the ampholyte being part of the composition may be both synthetic and derived from natural products. Those derived "naturally", the so called fatty alcohols, are usually produced by the reduction of fatty acids or fatty acid esters obtained from vegetable oils, such as coconut oil, palm oil, soybean oil, linseed oil, maize oil or castor oil; animal oils or fats, such as fish oil, whale oil, tallow or lard. As examples of suitable alcohols the following should be mentioned: octyl alcohol, decyl alcohol, lauryl alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, eicosyl alcohol, oleyl alcohol or eicosenyl alcohol. Synthetic alcohols are preferably produced according to the Ziegler process or by the Oxo process. Most of the alcohols produced by means of the Oxo process have a more or less branched carbon chain, so that in this case a great number of isomers are possible. The physical and chemical properties of these alcohols are very similar to the properties of the straight chain primary alcohols.

In addition to aliphatic alcohols cycloaliphatic and aromatic hydroxyl compounds may also be used as the starting product. Suitable cycloaliphatic alcohols are cyclohexanol, cycloheptanol, cyclooctanol, cyclododecanol and cyclohexadecanol. Among suitable aromatic hydroxyl compounds synthetically produced mono- and dialkyl substituted phenols, such as octylphenol, nonyl-

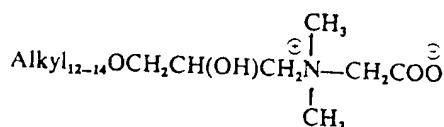
phenol, dodecylphenol, hexadecylphenol, dibutylphenol, dioctylphenol and dinonylphenol, should above all be mentioned.

Suitable amines are dimethyl amine and diethyl amine which both are commercially available. The monohalogenocarboxylic acid should be α -halogenated for obtaining a fast reaction with the tertiary amine. Examples of preferred α -halogenocarboxylic acids are monochloroacetic acid, α -monochloropropionic acid and α -monochlorobutyric acid. Among the aminocarboxylic acids which may be used according to the invention the α -aminocarboxylic acids are the most suitable, even if, for example, β -aminocarboxylic acids may be used in principle. Especially, among the amino acids dimethylglycine, dimethylalanine and dimethylvaline should be mentioned.

In detail the preparation of the ampholytic compounds may be illustrated by the following experiments.

15 Into a glass flask provided with stirrer, heating device and reflux cooler there were introduced 200 g (1 mol) of a mixture of 55% lauryl alcohol and 45% myristyl alcohol which was heated to 75°C, whereupon 2 g SnCl_4 and 101 g (1,1 mol) epichlorohydrin were added. The addition of the latter went on during 1 hour. Then the temperature was raised to 125°C with continued stirring and the mixture was held at this temperature during 2 hours. Residual epichlorohydrin was removed by vacuum treatment of the product which consisted of a slightly yellow-coloured liquid. With stirring 134 g sodium dimethylglycine and 344 g monoethyleneglycol were heated to 125°C and then had the glyceryl ether added thereto dropwise during 25 minutes. After another 10 minutes at 125°C the reaction was interrupted and the mixture which essentially consisted of NaCl and an ampholyte according to the invention was hot-filtered, a clear slightly yellow liquid being obtained. The rate of reaction of the chloroglyceryl ether with dimethylglycine was 98%.

20 The final product obtained had the formula

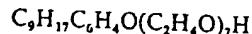


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wherein Alkyl_{12-14} designates a myristyl or lauryl group.

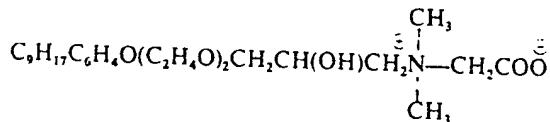
The synthesis below is still another detailed example of the preparation of ampholytes according to the invention.

To 1 mol nonylphenol ethylene oxide adduct of the formula



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there was added 1,1 mol epichlorohydrin according to the same method as stated above. Of the glycerylether product obtained 80 g (0,2 mol) were mixed with 67,5 g of a 40 per cent aqueous solution of dimethylamine (0,6 mol). The reaction mixture was allowed to stand 2 hours at 150°C. Hydrochloric acid formed was neutralized with 8,32 g NaOH, whereupon the mixture was transferred to a separatory funnel and the top phase containing the tertiary amine was separated. Dimethylamine dissolved in the amine phase was driven off by vacuum evaporation. The product was analyzed by titration with perchloric acid in glacial acetic acid and with sodium lauryl sulfate at pH 11, and was found to consist of 95% tertiary amine but no quaternary compounds. Of the tertiary amine 58 g were dissolved in 61 g water and 26 g ethyleneglycol. The mixture was heated to 70°C and then there was added dropwise during 1 hour a 40 per cent solution of monochloroacetic acid in water neutralized with sodium hydroxide so that the total quantity of chloroacetic acid added amounted to 15,7 g. After another 1 hour the temperature was raised to 90°C. The reaction was interrupted after 3 hours at this temperature when 97% of the tertiary amine had reacted and 99% of the theoretical amount of chloride ions had been formed. The product, which consisted of



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had a syrupy consistency at room temperature.

In addition to the ingredients stated the composition according to the invention may also contain a long series of additives common in detergent compositions. Examples thereof are bleaching agents, such as sodium perborate, sodium percarbonate, sodium perpyrophosphate and sodium persulfate; dirt suspending agents, such as carboxymethylcellulose and polyvinylpyrrolidone; fillers, such as sodium sulfate, sodium chloride and carbamide; buffering substances, such as mono phosphates, carbonates, borates and silicates in the form of their alkali metal salts and potassium and sodium hydroxide; optical whiteners; enzymes; dyes; bactericides; corrosion inhibitors, such as various types of alkyl-ether phosphates; wetting agents; softeners; perfumes etc. The composition may also contain surface-active components of anionic and/or cationic character, such as soaps, alkyl sulfates, alkylether sulfates, alkylaryl sulfonates, alkylsulfonates, alkenyl sulfonates, primary alkylamide salts and quaternary ammonium compounds with 1 or 2 long alkyl groups.

The compositions according to the invention are primarily suited for washing or cleaning materials, such as textiles, metals, plastics, leather, wood, stones, glass, china, painted surfaces etc., both in the domestic sector and in the industry. Since the compositions are low-foaming, they are especially suitable for use in the case of machine washing or machine washing-up or other applications where a high degree of foaming should be avoided.

The following examples are intended to further illustrate the present invention:

Example 1.
A detergent composition was formulated from the components mentioned below:

Ingredients	Parts by weight
Ampholyte	
Decyl-OCH ₂ CH(OH)CH ₂ N(CH ₃) ₂ CH ₂ COO [⊖]	2
Ampholyte	
Cetyl-O(C ₂ H ₄ O) ₄ CH ₂ CH(OH)CH ₂ N(CH ₃) ₂ CH ₂ COO [⊖]	2
Non-ionic surfactant	
Lauryl-, myristyl-O(C ₂ H ₄ O) ₈ H	6
Potassium pyrophosphate	12
Propyleneglycol	12
Water	66

The detergent composition obtained consisted of a clear, very mobile liquid within the temperature interval -4°C to +45°C. Its foam stability in water was determined in an equipment according to Fries which simulates the mechanical working of a washing agent solution in a cylinder washing machine. The method has been described in Seifen-Ole-Fette-Wachse, No. 25/65, p. 913—917. "Messmethode zur Testung gesteuerter Schäume". For a comparison the same test was carried out, on one hand, on a commercial washing agent specially composed for washing at 60°C, on the other hand, an ampholyte composition without non-ionic surfactant. The compositions of compared products were the following:

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Composition	Water hardness	Concentration of washing agent	Washing effect % washed off
Commercial product	2,8 16,8	5 10	66,0 77,0
Ampholyte composition accord. to invention	2,8 16,8	5 10	85,1 83,1
Ampholyte without non-ionic surfactant	2,8 16,8	5 10	78,5 78,6

From the results it is apparent that the composition according to the invention shows substantially higher cleaning effect than the two compositions of comparison.

To compare the washing effect of the commercial product and the ampholyte composition according to the invention on pigment dirt (substantially silicates) a washing experiment was carried out in a Terg-O-Tometer at a temperature of 40°C, a water hardness of 2,8°dH and a concentration of washing agent of 5 g/l. As material to be washed artificially soiled cotton fabric from Wäschereiforschung, Krefeld, Western Germany, was used. The reflectance of the fabric was measured before and after washing, and the measurements were converted according to Kubelka-Munk's formula $K/S = (1-R)^{2,2}/R$, wherein R is the reflectance. In other respects, see W. G. Catler and R. C. Davis; Detergency, Theory and Test Method, part 1, New York 1972, p. 387-392. The washing effect was expressed as the relative reduction of K/S, the following results being obtained:

Composition	Washing effect
Commercial product	47,2
Ampholyte composition accord. to invention	50,8

Thus, the composition according to the invention removed also pigment dirt better than the commercial product.

In the same way as in the case of the cotton fabric soiled with pigment a washing experiment was carried out at 60°C with cotton fabric soiled with cocoa, said fabric being obtained from Eidgenossische Materialprüfungsanstalt, St. Gallen, Switzerland. The following results were obtained.

Agent	Washing effect
Commercial product	23,0
Ampholyte composition accord. to invention	26,5

From the results it is apparent that the washing effect also in this case was clearly better for the composition according to the invention than for the commercial product of comparison.

Example 2.

A liquid washing agent was formulated of the same ingredients as in Example 1, but with the exception that the potassium pyrophosphate had been replaced by an equivalent quantity of sodium nitrilotriacetic acid. The washing effect of the composition obtained was then tested in exactly the same way as has been described in Example 1, on cotton fabric soiled with either silicate pigment or cocoa. In this case a washing effect of no less than 52,2% or 28,7%, respectively, was obtained. These values which can be directly compared with those in Example 1, show that the composition according to the invention has very good washing power.

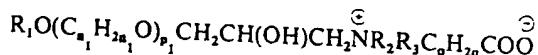
Example 3. A liquid washing agent was formulated of the following ingredients.

Ingredients	Parts by weight
Ampholyte	
Nonylphenol-O(C ₂ H ₄ O) ₂ -CH ₂ CH(OH)CH ₂ N(CH ₃) ₂ -CH ₂ COO	5
Non-ionic surfactant	
Nonylphenol-O(C ₂ H ₄ O) ₂ -H	5
N-(2-hydroxyethyl)-iminodiacetic acid	12
Ethyleneglycol	6
Propyleneglycol	6
Water	66

The washing effect of the composition obtained was thereupon tested on cotton fabric soiled with silicate pigment or cocoa. The testing which was carried out in exactly the same way as in Example 1 resulted in a washing effect of 51,2% or 28,1%, respectively, which shows that also this composition according to the invention had excellent washing power.

WHAT WE CLAIM IS.—

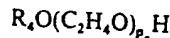
1. A liquid detergent composition comprising a sequestering agent, water, at least one non-ionic surfactant and at least one amphotolyte of the general formula:



wherein R₁ represents an aliphatic or cycloaliphatic group with 6—22 carbon atoms or an aromatic group having one or more alkyl substituents with a total of 4—18 carbon atoms in the alkyl substituents; R₂ and R₃, which may be the same and/or different, each represents an alkyl group of 1—3 carbon atoms; n₁ is 2 and/or 3 and/or 4; p₁ is O or an integer from 1 to 10; and q is 1, 2 or 3.

2. A composition according to claim 1, wherein the weight ratio of the sequestering agent, the non-ionic surfactant, the amphotolyte and water is

4-23-1-20-1-15-40-90. The composition, the ampholyte and water is
3. A composition according to claim 2 wherein the ratio is
6-20-2-15-1-10-45-80.
4. A composition according to any one of the preceding claims wherein the
non-ionic surfactant has the general formula:



wherein R₄ is an aliphatic or cycloaliphatic group with 8—20 carbon atoms or a mono or di alkyl phenyl group with a total of 4—18 carbon atoms in the alkyl substituents; and p₃ is a number from 5—30.

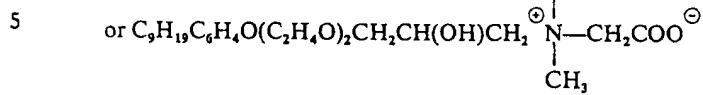
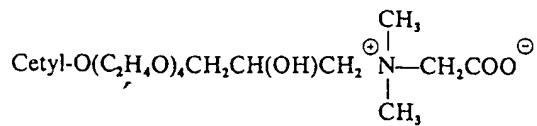
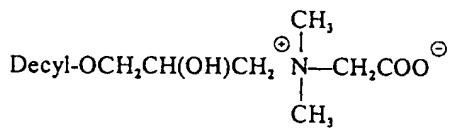
6. A composition according to claim 4 wherein n_1 is 5 to 20.

6. A composition according to claim 4 wherein p₃ is 5 to 20.

7. A composition according to any one of the preceding claims wherein the amphotolyte is one in which the nitrogen atom and the carboxylic group are linked to the same carbon atom and in which R_2 and R_3 each represents a methyl group.

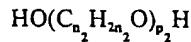
7. A composition according to any one of the preceding claims, wherein a is 1 and n_1 is 2.

8. A composition according to any one of the preceding claims, wherein the ampholyte is



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9. A composition according to any one of the preceding claims wherein it contains an alkylene glycol of the general formula:



10 wherein n_2 is 2, 3 and/or 4, and p_2 is an integer of 1 to 10.

10. A composition according to claim 9 wherein n_2 is 2 and/or 3 and p_2 is an integer of 1—5.

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11. A composition according to claim 1 substantially as hereinbefore described.

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